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Experiments with the Ammonium Amalgam.

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EXPERIMENTS WITH THE AMMONIUM AMALGAM.

BY

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THE existence of the hypothetical radical NH_4 depends less upon the characteristics of its so-called amalgam than upon the parallelism of its salts with those of the alkalies. If, from these analogies, we accept the metallic nature of ammonium, it will be difficult to avoid assigning a similar character to the radicals of all of the organic bases; and especially to those which, like the compound ammonias, have an alkaline reaction and possess physical and chemical properties so like ammonia.

If such be the inference, we must admit numerous *compound metals*, which exists only in certain states of combination of their elements. The assumption of the elementary nature of a metal is destroyed and the ideas of the alchemists are revived; for if NH_4 be a metal and NH_3 be not one, why may not other metals, esteemed elements, be also compounds.

In examining the so-called ammonium amalgam one is interested at the great resemblance which it bears to the amalgams proper in its physical properties. The mercury has lost its fluidity or mobility, and, at the same time, its relations of cohesion and adhesion are very sensibly altered. It no longer coheres powerfully; but adheres to, or wets, platinum, iron and other metals, like the potassium or sodium amalgam. When left to

itself, the swollen mass shrinks, and gradually resolves itself into $\text{NH}_3(\text{NH}_4\text{O})\text{H}$ and Hg , because (as it is usually explained) NH_4 has a great tendency to fall apart into NH_3 and H . This explanation might be satisfactory when applied to the difficulty of isolating NH_4 , as from any of its salts; but is not so in the case before us.

If ammonium falls apart thus readily in the presence of mercury, why does it combine with it at all to be decomposed in the very act of union? If it be said that in NH_4Hg the NH_4 has so great a capacity for oxydation that it at once decomposes water, with the formation of NH_4O and H ; still why should NH_4 unite with the mercury, *which is not as near to it as, or at least no nearer than, the water?* In reflecting upon the phenomenon, I conceived the idea that there is really no amalgam of ammonium formed; but, in the reaction, the sodium decomposes the water, evolving hydrogen, and forming caustic soda, which in its turn sets free ammonia from the chlorid, the mercury being also liberated. Thus $\text{NH}_4\text{Cl} + \text{HO} + \text{Hg Na} = \text{NH}_4\text{O} + \text{H} + \text{NaCl} + \text{Hg}$. At the same time the molecules of the mass are altered in their capacity for cohesion by catalysis, polarity of atoms, or some unknown cause, so that the bubbles of gas are retained, and swelling takes place.

Without the assumption of an unknown cause, the swelling may be accounted for by admitting that the evolution of gas brings portions of the sodium amalgam out of contact with the solution, and the mass thus remains pasty enough to retain the gas bubbles of hydrogen and ammonia for a while. The swelling may subside by reason of the final oxydation of this residual sodium amalgam.

By the kindness of Professor Henry, the opportunities of the laboratory of the Smithsonian Institution were afforded me in the winter of 1863-4, to perform the following experiments upon this subject.

The ammonium amalgams were obtained by the agency of the sodium amalgam, which was itself prepared by warming distilled mercury and projecting sodium therein. By varying the proportion of mercury, the sodium amalgam was obtained either quite fluid, pasty, in acicular crystals, or quite hard. The ammonium amalgam was prepared from all of these alloys; but when a hard amalgam was used in the experiment, the ammonium amalgam formed upon the surface of the lump and proceeded gradually to the inside, and the swelling was not so great at the close of the reaction. The more fluid the sodium amalgam was, the more readily did the swelling take place.

Ex. 1°. Sodium amalgam projected into dilute solutions of sulphuric or hydrochloric acids, or into an aqueous solution of potassa, decomposes water, but not violently. The mercury does

not swell, but this phenomenon takes place immediately if a little solution of sal-ammoniac be added. It is not, therefore, merely hydrogen, (itself a hypothetical metal), in the nascent state which occasions the swelling.

Ex. 2°. Sodium amalgam in a solution of ammonia decomposes water without swelling; but this phenomenon ensues immediately if a drop of sulphuric or hydrochloric acid be added. Hence, hydrogen in the nascent state and ammonia in the *condition of stable equilibrium* do not produce the swelling. To effect this the ammonia itself must also be nascent.

Ex. 3°. When the ammonium amalgam is made in a test tube containing a thermometer, a rise of temperature of from 2° to 3° C. is indicated during the swelling. The temperature falls at the completion of the swelling. If the turgidity subsides by reason of the great affinity of NH_4 for the oxygen of the water, decomposing the latter with the evolution of hydrogen, an elevation of temperature ought to be maintained until the NH_4 has become converted into NH_4O .

Ex. 4°. If a test tube be filled with a solution of sal-ammoniac, inverted in a capsule containing the same salt, and a piece of sodium amalgam be introduced under the test tube, the ammonium amalgam is at once generated, with the constant evolution of hydrogen gas; the porous amalgam floats up to the surface of the liquid, and, subsiding after a while, gradually returns to mercury. From the time that the swelling is at its maximum until the mercury is restored to its pristine condition, there is but trifling increase of the volume of the gas, and this increase appears to be due to the minute particles of sodium amalgam which have been brought out of contact with the sal-ammoniac by reason of the turgescence. None of the gas in the test tube is absorbable by water; it is all hydrogen, and the sal-ammoniac remaining reacts strongly alkaline. The same phenomenon takes place when the amalgam is formed in a solution of sal-ammoniac in a capsule under a layer of naphtha. The presence of air, therefore, has no part in the subsidence of the swelled mass.

Ex. 5°. When the amalgam, having again sunk to the bottom of the capsule in the last experiment, is pressed with the finger against the vessel, under the naphtha, it has at first a pasty or smeary nature; but, apparently by the expression of hydrogen gas from its pores, it is very quickly restored to the ordinary condition of mercury.

Ex. 6°. When the ammonium amalgam is squeezed through a piece of muslin it is *immediately*, and without change of temperature, or other evidence of affinity, resolved into mercury.

Ex. 7°. If a drop of sal-ammoniac solution be placed upon a plate of glass, a lump of soft sodium amalgam be added, and another plate of glass be pressed upon the whole, the ammoni-

um amalgam formed cannot swell, but expands laterally, assuming a reticular appearance by reason of the many gas bubbles which in fact thus become perceptible.

If a lump of ammonium amalgam, already in the swollen condition, be pressed between two plates of glass, it is spread out into a thin perforated film resembling lace.

Ex. 8°. If a piece of spongy platinum be heated and stirred into smelted sodium amalgam, the latter fills the pores of the platinum sponge, and coats it uniformly. A piece of this compound in contact with a solution of sal-ammoniac, evolves hydrogen and ammonia, but does not swell; nor does a globule of liquid mercury, expressed from the mass, exhibit any of the characters of the ammonium amalgam.

Ex. 9°. A piece of ammonium amalgam was wiped gently with filter paper and placed in naphtha. After a little while, (to permit any adherent water to be decomposed), a test tube full of naphtha was inverted over it, the evolution of hydrogen gas continued as the amalgam shrank, and when, after the lapse of an hour, the mercury was restored to its usual condition, a bubble of gas, equal in volume to the globule of mercury, was collected.

Ex. 10°. If a drop of sodium amalgam be heated upon a glass plate, then touched with a drop of sal-ammoniac solution, it at once swells to the full size of an ammonium amalgam which would have required several minutes if the reaction had taken place in the cold.

Ex. 11°. The sodium amalgam decomposes cold water with comparative slowness; in boiling water a rapid evolution of gas takes place, although some time is required to fully oxydize the sodium. Boiling solution of aqua ammonia acts like boiling water. In none of these cases does any swelling take place, but this phenomenon is manifested immediately if to the boiling aqua ammonia a few drops of carbonate of ammonia be added.

Ex. 12°. The ammonium amalgam is formed with apparently equal facility, employing the solutions of the following ammonia salts:—Chlorid, oxalate, sulphate, and *bi-sulphate*; the characteristics of the amalgam thus formed being alike. The reaction with *bi-sulphate* of ammonia is instructive, showing the formation of the amalgam in the presence of an acid which facilitates the decomposition of water by certain metals. If a piece of reddened litmus paper be saturated with solution of *bi-sulphate* of ammonia, and a piece of sodium amalgam be dropped thereupon, the formation of the ammonium amalgam takes place as usual, and the evolution of the ammonia neutralizes the acid, producing an alkaline reaction upon the paper under the mass.

Ex. 13°. The ammonium amalgam cannot be formed with solution of nitrate of ammonia. With this reagent a very rapid evolution of gas takes place, and a globule of mercury remains. In this reaction there are no indications of hyponitrous or nitrous acids, and a drop of sulphid of ammonium added to the resulting liquid produces no coloration, except in a film upon the globule of mercury. If a drop of fluid sodium amalgam be projected into a drop of solution of sal-ammoniac upon a glass plate, the ammonium amalgam is formed rapidly; but a few drops of solution of nitrate of ammonia poured upon the swelled mass, reduce it instantly, and without the evolutions of nitrous fumes, to the condition of ordinary mercury.

Ex. 14°. By the kindness of M. Carey Lea, Esq., who furnished me with some of the salt, I have acted upon the sodium amalgam with solution of oxalate of methylamine. A slight turgescence is exhibited in this reaction, but not nearly to so great an extent as with oxalate of ammonia. The globule of methylamine amalgam pressed between glass plates manifests a reticulated appearance from gas bubbles, but to a less degree than in the case of ammonia salts. Hydrogen and methylamine are evolved.

Ex. 15°. *With the battery.*—The ammonium amalgam was formed by the battery, using different ammonia salts in contact with mercury at the negative pole.

The general characteristics of the amalgam thus obtained were the same as when sodium was employed.

With a Smee battery of six pairs, of which each zinc plate measured 3×5 inches, the amalgam was obtained in small quantities; but ten of Bunsen's elements were required to obtain sufficient to study its properties.

By the electrolysis of a solution of sal-ammoniac contained in a U tube, which was furnished with a porous diaphragm of filter paper, decomposition took place rapidly with either of the batteries; hydrogen and ammonia appearing at the negative pole, and nitrogen, chlorine, and hydrochloric acid at the positive pole. No formation of chlorid of nitrogen was detected in the reaction.

The amalgam did not form with mercury in the negative branch of the U, the decomposition then being the same as without the metal.

The electrolysis of carbonate of ammonia yielded similar results, carbonic acid being evolved.

With solution of nitrate of ammonia in a U tube, hydrogen and ammonia appeared at the negative pole, and nitric acid and oxygen at the positive electrode. A small quantity of the gases collected at the positive pole were absorbed by water. If a globule of mercury be placed in a cup-like depression in a

moistened lump of sal-ammoniac or carbonate of ammonia and be connected with the negative pole, the circuit being completed through the salt, the ammonium amalgam is formed while the current is passing.

If a piece of filter paper be placed upon a glass plate, and be moistened with a solution of carbonate of ammonia containing lumps of the salt, and if upon the paper a globule of mercury be deposited, the amalgam is beautifully manifested when the current of a ten cell Bunsen battery is passing through the mercury and paper, the metal being in contact with the negative pole. The amalgam swells out in a dendritic form, tending toward the positive pole, and maintaining its condition while the current lasts. Upon breaking the connection the swelled mass shrinks gradually. At all times, until restored to the condition of mercury, the amalgam exhibits numerous and minute gas bubbles when pressed between glass plates.

If, during the passage of the current, a glass plate be pressed upon the amalgam, it is flattened into a thin plate or film. By this means the swelling is prevented, *and the ammonium amalgam is not formed.* This result appears to be conclusive as to the non-existence of the ammonium amalgam, for, if it exist, it should be maintained in a *film* as well as in a *globule* as long as the current is passing.

The so-called ammonium amalgam could not be formed by the electrolysis of nitrate of ammonia, and a few drops of a solution of this salt causes the swelling to subside in ammonium amalgam already formed by the action of the battery upon sal-ammoniac, or carbonate of ammonia, in contact with mercury.

If spongy platinum, imbued with mercury, be placed in contact with the negative pole of the battery, and the current be passed through either a solution of sal-ammoniac, or one of carbonate of ammonia to the positive pole, no swelling takes place, even though a large globule of mercury adhere to the sponge; but violent ebullition of gas is manifested.

This is a very instructive experiment. The sponge of platinum cannot act by reason of fine pores, for they are all filled with mercury. The prevention of the amalgam formation must lie in the nature of the platinum itself; it is a catalytic or contact action.

From these experiments it would seem that:—

1st, The so-called ammonium amalgam is *not* an alloy of mercury and ammonium;

2d, The swelling of the mass in the phenomenon is due to the retention of gas bubbles; and,

3d, The coherence of the gases and liquids concerned is changed from a normal condition, exhibiting phenomena which may be classed with those of catalysis.

